

Purification of Lignocellulose Hydrolysate by Org-Attapulгите/(Divinyl Benzene-Styrene-Methyl Acrylate) Composite Adsorbent

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The purification of lignocellulose hydrolysate is crucial for the efficient conversion of lignocellulose. In this study, weak polar poly(styrene-divinyl benzene-methyl acrylate) (PSDM) and composite adsorbent org-attapulгите/poly(styrene-divinyl benzene-methyl acrylate) (PSDM-T) were prepared *in situ* by suspension polymerization for the detoxification of mixed hydrolysate. The org-attapulгите (O-A-T) used was functionalized with the silane coupling agent KH-570. The effect of O-A-T mass on PSDM-T was investigated. The results showed that the addition of a moderate mass of O-A-T improved the pores of PSDM-T and adsorption abilities. Furfural and 5-HMF (FS), total weak acids (WA), and soluble lignin (SL) were removed simultaneously. The adsorption capacities of PSDM-T for FS, WA and SL were 37.5 mg/g, 34.3 mg/g, and 87.7 mg/g, respectively. Correspondingly, their removal extents (*R*) were 72.6%, 18.1%, and 52.3%. The adsorption abilities of the PSDM-T for mixed hydrolysate was better than AB-8 (a commonly-used adsorption resin). The total decolorization rates (*D*) greater than 63%. The adsorption property retains high adsorption activity after two cycles.

Keywords: Lignocellulose hydrolysate; Purification; Preparation; Composite adsorbent

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INTRODUCTION

Lignocellulosic biomass is the most abundant and bio-renewable resource on the earth. Over the years, various products have been generated from lignocellulose biomass using biochemical technologies; these products include bioethanol (Binod *et al.* 2010), biobutanol (Dürre 2007), and carbon materials (Maiti *et al.* 2008). The utilization and conversion of lignocellulose for such products involves a series of processes (Binod *et al.* 2010).

A wide range of technologies, such as fermentation, anaerobic digestion, and mechanical extraction, *etc.*, have been developed and applied to the conversion of lignocellulosic biomass into bio-products (McKendry 2002; Kaparaju *et al.* 2009). Among these conversion technologies, fermentation shows great advantages and has become a common method. To ensure efficient conversion, an appropriate pretreatment process is required, and hydrolysis by dilute acid is an effective and economic pretreatment method (Chen *et al.* 2011). Through dilute-acid or enzymatic hydrolysis, lignocellulose is transformed into hydrolysate which consists not only of monosaccharides available to the fermenting microorganism, but also inhibitors that are harmful to fermentation (Palmqvist

and Hahn-Hägerdal 2000), including weak acids, furan derivatives, and a portion of soluble lignin. The presence of these inhibitors during the fermentation process may seriously impact the efficiency of production (Sainio *et al.* 2011). As a result, the detoxification of hydrolysate is advised as a way to remove inhibitors before fermentation.

There are various methods for removing inhibitors, including biological, physical, and chemical methods, and combinations thereof. Among these methods, adsorption is a convenient and effective technique due to simplicity of the processes, low cost, and wide practicability. The commonly-used adsorbent including activated charcoal (Larsson *et al.* 1999), ion exchange resins combined with alkali (Zhuang *et al.* 2009; Chandel *et al.* 2011), and zeolites (Ranjan *et al.* 2009). However, the activated charcoal and zeolites are relatively costly in industrial production, while ion exchange resins need a large amount of alkali to achieve a set pH value and a high amount chemical solvent for regeneration. On the other hand, in contrast to ion exchange resins, certain polymeric adsorption resins have no ion-exchange groups, but do have rich porous networks and great adsorption capacities. Their regeneration is comparatively easy, requiring only ethanol. For this reason, numerous applications of these adsorption resins have been reported (Liu *et al.* 2010; Lin *et al.* 2012).

Attapulгите (also known as palygorskite) is an unusual magnesium aluminum silicate mineral, demonstrating outstanding absorptive properties due to its unique porous structure, in addition to low cost and easy availability (Haden and Schwint 1967). It has been applied to the purification of oil systems (Liu *et al.* 2008) and to the adsorption of p-nitrophenol (Sarkar *et al.* 2012), tannic acid (Wu and Chen 2013), and toxic metals (Liang *et al.* 2013; Sheikhhosseini *et al.* 2013). To the best of our knowledge, no report has described the application of attapulгите for the removal of fermentation inhibitors from lignocellulosic hydrolysate. In this article, the raw attapulгите was treated with inorganic acid and KH-570. Then, a weak polar adsorption resin poly(styrene-methyl acrylate-divinyl benzene) (PSDM) and org-attapulгите/poly(styrene-methyl acrylate-divinyl benzene) (PSDM-T) composite adsorbent was prepared *in situ* in order to prepare the desired adsorbent for the purification of lignocellulose hydrolysate. The effects of feed time and mass of org-attapulгите (O-A-T) on the properties of adsorbents were investigated.

EXPERIMENTAL

Materials

Styrene (St, 98.0%), toluene (TOL) and methylene blue were obtained from Tianjin Damao Chemical Company. Methyl acrylate (MA, 98%), divinyl benzene (DVD, 80%), paraffin liquid (PL), benzoyl peroxide (BPO, $\geq 98\%$), polyvinyl alcohol AH-26 (PVA, 97.0 to 98.0 mole%), sodium chloride (NaCl, $\geq 99.7\%$), silane coupling agent (KH-570), and ethanol ($\geq 99.7\%$) were obtained from Chinese Chemical Company and were of analytical grade.

AB-8 resin, as a reference, was bought from Anhui Samsung Resin Technology Co., Ltd. (Anhui, China). Before utilization, it was soaked in ethanol for several hours and washed with deionized water until the ethanol was removed. The attapulгите was purchased from Jiangsu AoTeBang international Co. in China, with a particle size $\leq 0.075\text{mm}$ (200 mesh). Bagasse hydrolysate, straw stalk hydrolysate and corncob hydrolysate were provided by Zhongke New Energy Technology Co., Ltd. (Yingkou, China) and mixed in one solution.

Methods

Syntheses of PSDM and PSDM-T

The PSDM was synthesized using the suspension synthesis method. The process was as follows: (a) 7.0 g of dispersant PVA was dissolved into 140 g of deionized water at 95 °C in a 500-mL three-necked flask; (b) 8.0 g of NaCl and several drops of methylene blue solution were added into the flask as dispersing and stabilizing auxiliaries when the temperature decreased to room temperature; (c) the oil phase-materials including 10.0 g of monomers, 30.0 g of DVB, and 40.0 g of porogen (TOL: PL = 1:1), were mixed in a 250-mL beaker and poured into the flask; (d) the temperature was raised gradually from room temperature to 80 °C within 5 h at a certain stirring speed, and then maintained at 80 ± 2 °C for 3 h; (e) after the reaction, the sample was extracted using ethanol to remove porogen.

The preparation of PSDM-T was an *in situ* process, mainly involving two parts. (1) Preparation of O-A-T. The weighed attapulgite and 10~20 g of ethanol solution of KH-570 (1%, w/w) were stirred for approximately 40 min. The mixture was dried in an oven at 80 °C and dissolved with TOL before using; (2) Composite synthesis. The process proceeded according to the above-mentioned syntheses of PSDM steps (a), (b), and (c). The O-A-T was added into the reactor in three conditions: (i) the temperature reached 75 ± 1 °C; (ii) the temperature reached 80 °C; and (iii) the temperature had remained at 80 °C for 1 h. After reacting about 3 h in the flask, the bead (PSDM-T) was removed and extracted in a Soxhlet extractor for 12 h.

Purification of mixed lignocellulose hydrolysate and adsorbent regeneration

The weighed adsorbents (equal to 2.0 g of dried adsorbent) and 40.0 g of original mixed hydrolysate (solid-liquid of 1:20) were added into 150-mL conical flasks. After 2 h static adsorption in a shaker under 150 rpm at 28 °C, the liquid was analyzed by HPLC and UV-Vis spectroscopy. The adsorbents were separated and regenerated later. After regeneration, the adsorbents were utilized again for the purification of the original mixed lignocellulose hydrolysate, and the results were analyzed. Two regeneration and adsorption experiments were then carried out.

Analysis method

The morphology of the resins and the composite adsorbent were observed using a scanning electron microscope (SEM, S-4800 Hitachi, Tokyo, Japan) operated at 2.0-kV, with an accelerating voltage 10.1 µA. The surface area of the samples was determined by means of nitrogen adsorption-desorption isotherms at 77 K in a conventional high vacuum volumetric system (Quantachrome, Boynton Beach, USA).

The concentrations of total sugars (TS, such as glucose, xylose, and arabinose), weak acids (WA, such as acetic acid, formic acid, and levulinic acid), furfural and 5-HMF (FS) were determined via HPLC with a Waters 2695 system (Milford, USA) equipped with a refractive index detector (Waters 2414), using 5 M sulfuric acid as an eluent. The soluble lignin content was calculated using the following equations (Gouveia and Souto-Maior 2009),

$$C_L = 4.187 \times 10^{-2}(A_L - A_{PD}) - 3.279 \times 10^{-4} \quad (1)$$

$$A_{PD} = C_F \cdot \epsilon_F + C_{HMF} \cdot \epsilon_{HMF} \quad (2)$$

where C_L is the soluble lignin (SL) concentration (g·L⁻¹); A_L is the absorbance of adjusted (pH = 12, 6 mol·L⁻¹ NaOH) and diluted (distilled water) hydrolysate at 280 nm, less than

1.0; C_F and C_{HMF} are the concentrations of furfural and 5-HMF; ε_F and ε_{HMF} are the absorbance of furfural and 5-HMF at the wavelength of 280 nm, 14.685 $\text{m}^2 \cdot \text{g}^{-1}$ and 11.40 $\text{m}^2 \cdot \text{g}^{-1}$, respectively.

The adsorption capabilities (Q_e) of the adsorbent were calculated using Eq. 3,

$$Q_{ie} = (c_{i0} - c_{ie})V / M \quad (3)$$

where Q_{ie} (g/g) is the equilibrium adsorption capacity of adsorbate i; c_{i0} (g/L) is the original concentration of adsorbate i; c_{ie} (g/L) is the final concentration of adsorbate i after being adsorbed; V (L) is the volume of the treated hydrolysate; and M (g) is the mass of the adsorbent used to adsorption purification.

The removal rates of inhibitors and loss of total sugars (TS) (R_i) were calculated using Eq. 4.

$$R_i = (c_{i0} - c_{ie})V \times 100\% / c_{i0}V \quad (4)$$

To observe the visual adsorption effect, the decolorization ratio D (%) was calculated using the follow equation,

$$D(\%) = (A_0 - A_t \times 100\% / A_0) \quad (5)$$

where A_0 is the initial absorbance of the hydrolysate at $\lambda = 540$ nm and A_t is the absorbance of the purified solution at $\lambda = 540$ nm. All the absorbance measurements of the liquid were made with a UV-Vis spectrophotometer (SP-752, Shanghai Spectrum Instrument Co., Ltd., Shanghai, China).

RESULTS AND DISCUSSION

The Effect of O-A-T Feed Time

To explore the appropriate feed time, the O-A-T (1.0 g) was added at different time intervals, the adsorbents prepared by adding O-A-T at 75 ± 1 °C, at the moment when the temperature had been at 80 °C for 1 h, and immediately at 80 °C were termed S1, S2, and S3 respectively. The surface morphology of resulting sample is shown in Fig. 1. The S1 sample was very viscous when the reaction was finished, and it appears as an uneven shape when dried (Fig. 1a). This result was likely due to the addition of O-A-T at 75 °C will hindered the polymerization of monomers, resulting in an immature and shapeless polymeric adsorbent.

In the S2 sample, the granules of O-A-T and polymer seemed to have separated, and the granules were significantly bigger and dimmer than those of the resin spheres (Fig. 1c). The O-A-T was probably added too late, while the resin polymer had developed into spheres, so the O-A-T could not to attach to the polymer effectively and consequently clustered. Compared with S1 and S2, S3 presented a uniform sphere (Fig. 1e). SEM images of these samples (Fig. 1b, d, and f) confirmed that the appropriate addition time of the O-A-T was at 80 ± 1 °C exactly. SEM micrographs of sample S3 demonstrated distinct and sufficient pores, while S1 and S2 were flocculent without pores. Because the feed time was dependent on temperature and temperature affects the material properties (Mohamed and Wilson 2012), different feed times meant changes in reaction temperature and changes in the formation process.

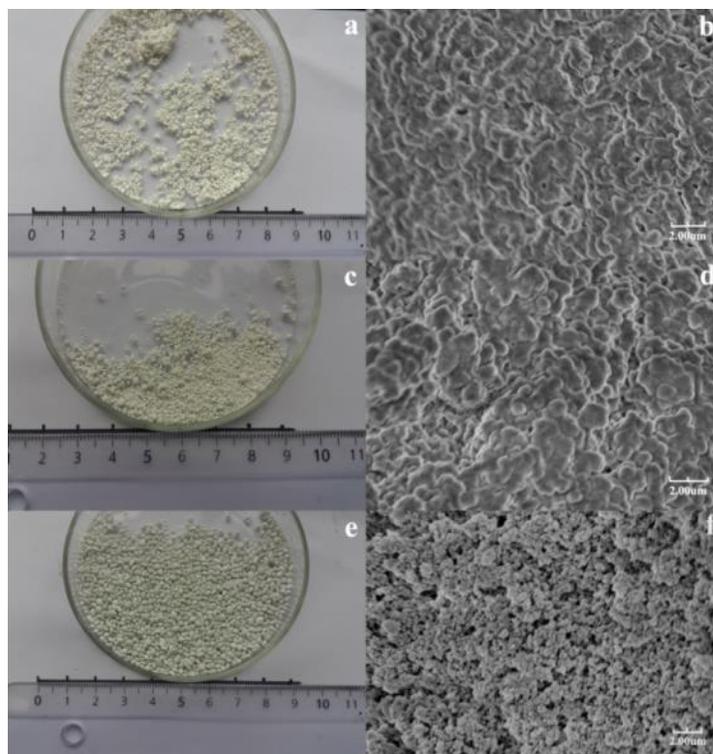


Fig. 1. Morphologies of the three samples prepared by addition of O-A-T at different feed times: (a and b) at 75 ± 1 °C, (c and d) when the temperature had been at 80 °C for 1 h, and (e and f) immediately at 80 ± 1 °C

The fermentable sugars solution was colorless, and the color of lignocellulose hydrolysate was largely caused by inhibitors, such as FS and SL. Therefore, the clarity of the hydrolysate is a visual parameter measuring purity, and to some extent the total decolorization rate can be used to determine the removal rate of the inhibitors. The decolorization rate of the hydrolysate by S3 (~65.9%) was far higher than by S1 (~1.7%) and S2 (~8.9%) (Fig. 2). Thus, the appropriate time of feeding was the moment when the action temperature reached 80 ± 1 °C.

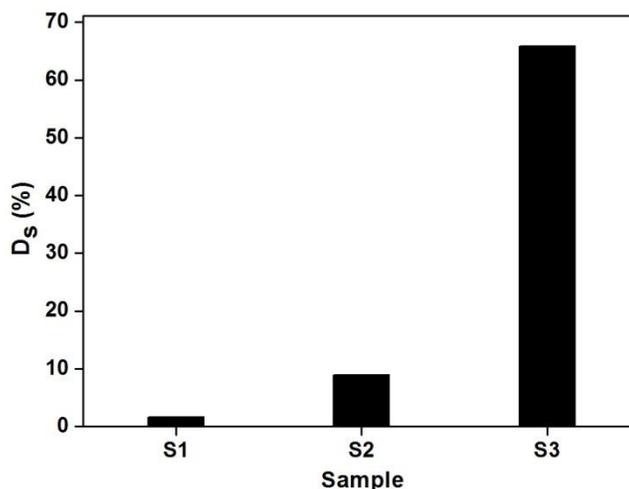


Fig. 2. The decolorization rate of mixed hydrolysate purified by S1, S2, and S3

Morphology and Porous Properties of Prepared Adsorbents

The morphology of AB-8 (Fig. 3a and b), PSDM (Fig. 3c and d), and PSDM-T3 (containing 3.0 g O-A-T) (Fig. 3e and f) are presented in Fig. 3. AB-8 and PSDM were globular and of uniform size at comparatively low magnification, while the PSDM-T3 had an irregular granular appearance. The PSDM-T3 was prepared in a liquid-liquid-solid three phases system instead of in two liquid phases (AB-8 and PSDM). Generally, the shape of the polymer was determined by the shape of the drops from the oil-in-water drop (Vivaldo-Lima *et al.* 1997). In the preparation process of PSDM-T, when the O-A-T was added and stirred by agitator, the shapes of the drops were altered by the solid. At higher magnification (Fig. 3 b, d, and f), inner porous structures of fractured adsorbent beads were observed. Similar to the polymeric resins (PSDM and AB-8), the PSDM-T3 had plenty of pores.

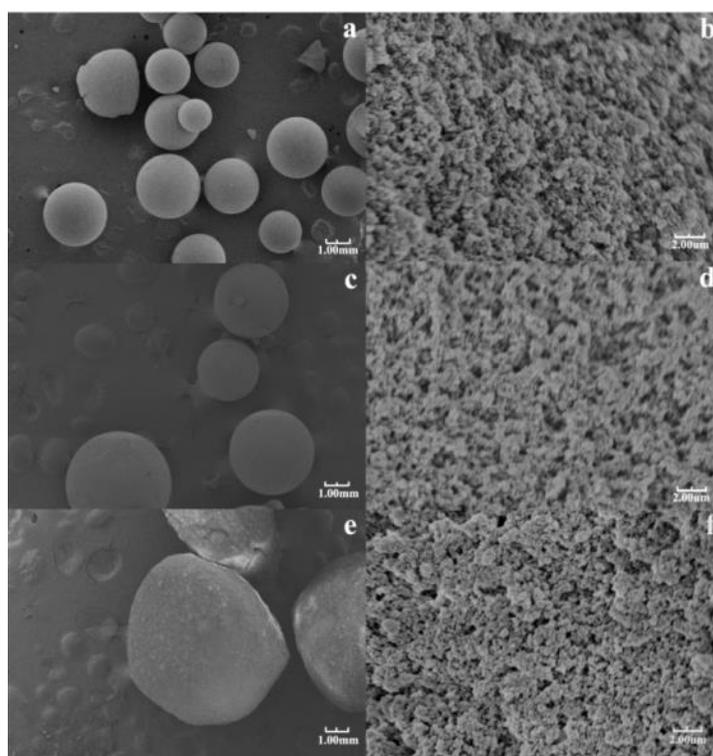


Fig. 3. SEM micrographs of AB-8 (a and b), PSDM (c and d), and PSDM-T3 (e and f)

Table 1. Pore Properties of Synthesized Resin (PSDM), Composite Adsorbent (PSDM-T3), and AB-8

Pore Parameter	S_{BET} (m^2/g)	S_{BJH} (m^2/g)	S_{V-t} (m^2/g)
PSDM	412.55	295.47	47.06
PSDM-T3	503.70	296.83	73.92
AB-8	447.77	298.27	21.23
O-A-T	124.19	124.19	0

The porous properties of O-A-T, AB-8, PSDM, and PSDM-T3 are listed in Table 1. The total specific surface area (S_{BET}) of the PSDM was lower than the AB-8, but the former had a larger micropore area (S_{V-t}). The value S_{BET} of the PSDM-T3 ($503.70 m^2/g$)

was larger than that of AB-8 and PSDM, which indicated that the addition of O-A-T increased the S_{BET} of the adsorbent. Compared with PSDM, the micropore area of PSDM-T3 increased about $34 \text{ m}^2/\text{g}$, while its mesopore area (S_{BJH}) was nearly unchanged. This indicated that the addition of O-A-T may decrease the macropore area of the adsorbent spontaneously.

Purification of Mixed Hydrolysate

Purification results of first-used composite adsorbents

The components of hydrolysate were divided into four groups: TS, WA, FS, and SL. The adsorption capacity (Q_i), removal rate (R_i), and total decolorization rate (D) were analyzed. Figure 4 shows the adsorption results of the FS, WA, SL, and TS by the PSDM-T with different masses of O-A-T. When the concentration of O-A-T in the PSDM-T increased, Q_{FS1} and R_{FS1} were gradually decreased, while Q_{WA1} and R_{WA1} , Q_{SL1} , and R_{SL1} , and R_{TS1} at first slightly increased and subsequently decreased. This was probably due to the interaction between PSDM-T and FS. The hydrogen bonding was formed between the C=O and C-O groups of PSDM-T and furfural and 5-HMF. The maximum adsorption capacities and removal rates of FS, WA, and SL reached 37.5 mg/g , 34.3 mg/g , 87.7 mg/g , 72.6% , 18.1% , and 52.3% , respectively, whereas the maximum loss of TS was as low as 8.6% . At the first usage and recycling, as one commonly-used weak polar adsorption resin, AB-8 (Table 2) performed similarly to PSDM-T5 (containing 5.0 g O-A-T) but inferior to PSDM-T1 and PSDM-T3, in correspondence with the porous properties.

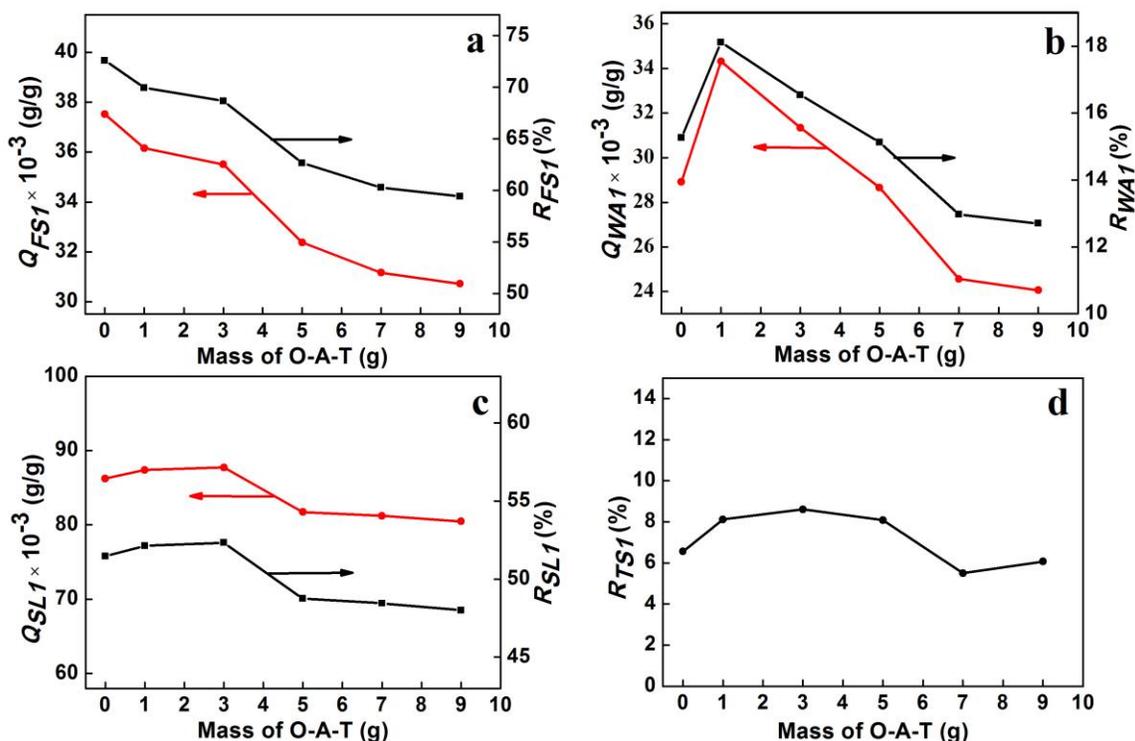


Fig. 4. The adsorption results for first-used PSDM-T with different mass of added O-A-T. (a) the adsorption capacity and removal rate of FS, Q_{FS1} and R_{FS1} ; (b) the adsorption capacity and removal rate of weak acids, Q_{WA1} and R_{WA1} ; (c) the adsorption capacity and removal rate of soluble lignin, Q_{SL1} and R_{SL1} ; (d) the loss of total sugars, R_{TS1} .

Table 2. Adsorption Results of Mixed Hydrolysate with AB-8, O-A-T and

Component		FS		WA		SL		TS	D (%)
		Q_{FS} (g/g)	R_{FS} (%)	Q_{WA} (g/g)	R_{WA} (%)	Q_{SL} (g/g)	R_{SL} (%)	R_{TS} (%)	
AB-8	First usage	32.7×10^{-3}	63.3	25.6×10^{-3}	13.5	83.3×10^{-3}	49.7	8.2	63.87
	R1	37.5×10^{-3}	68.4	16.4×10^{-3}	8.5	78.5×10^{-3}	46.9	7.3	65.05
	R2	38.4×10^{-3}	69.1	28.9×10^{-3}	14.9	83.1×10^{-3}	49.7	4.9	69.41
O-A-T	First usage	4.1×10^{-3}	8.0	6.2×10^{-3}	3.3	35.8×10^{-3}	21.4	1.2	30.41

R1, first time regeneration; R2, second time regeneration

Adsorbent regeneration

Re-using adsorbents to reduce costs is very important. For all PSDM-T samples, first-time and second-time regeneration processes were applied as part of the purification of the mixed lignocellulose hydrolysate (Figs. 5 and 6, respectively). The adsorption results were similar to the first-time purification. The differences in the adsorption capacities of the inhibitors between those purified by first-used and regenerated adsorbents were probably due to the instability of the hydrolysate; the component concentrations changed during storage.

In the first cycle, the adsorption capacities of the SL and TS by regenerated PSDM-T3 (83.5 mg/g) were lower than those by regenerated PSDM-T1 (86.5 mg/g), which probably was due to incomplete regeneration and hence residual inhibitors. Though the total adsorption quantity declined, the loss in nutrient sugars was simultaneously decreased to 6.6% of the maximum rate. Compared with the first cycle adsorbents, the second cycle adsorbents retained 99% of its original activity, with approximately 37.5 mg FS, 34.3 mg WA, and 87.7 mg SL per gram of adsorbent.

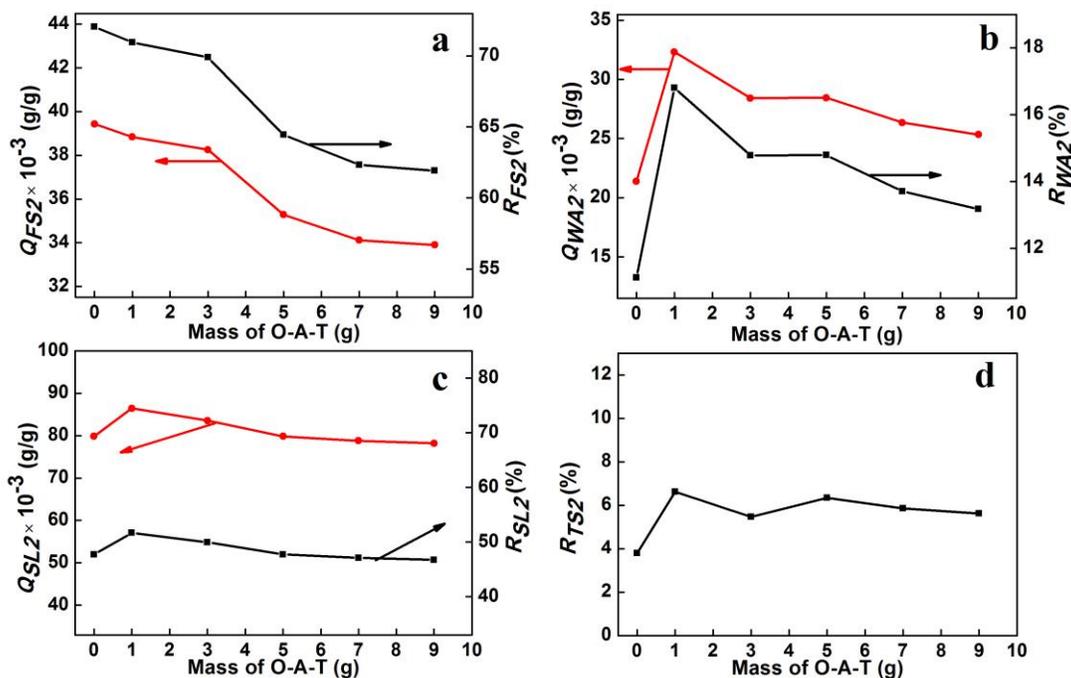


Fig. 5. The adsorption capacity Q and removal rate R for first-cycle regenerated PSDM-T with different mass of O-A-T. (a) FS, Q_{FS2} and R_{FS2} ; (b) weak acids, Q_{WA2} and R_{WA2} ; (c) soluble lignin, Q_{SL2} and R_{SL2} ; (d) the loss of total sugars, R_{TS2} .

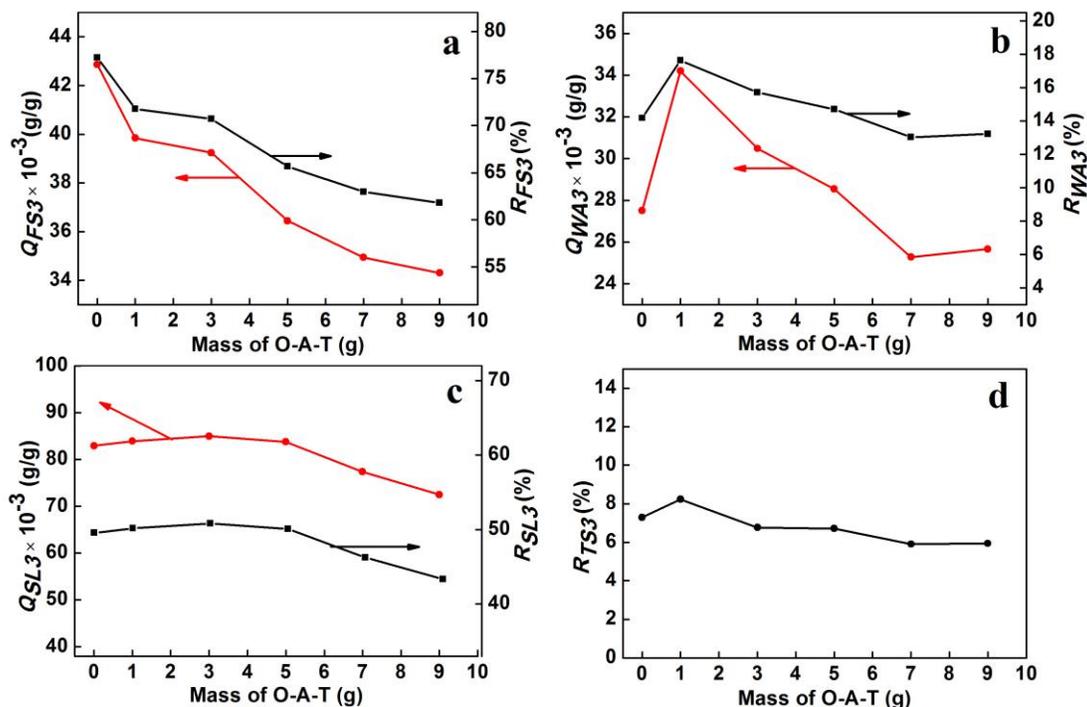


Fig. 6. The adsorption capacity Q and removal rate R for second-cycle regenerated PSDM-T with different masses of added O-A-T. (a) FS, Q_{FS3} and R_{FS3} ; (b) weak acids, Q_{WA3} and R_{WA3} ; (c) soluble lignin, Q_{SL3} and R_{SL3} ; (d) the loss of total sugars, R_{TS3} .

The total decolorization rates of the mixed hydrolysate by PSDM-T are shown in Fig. 7, which displays the first-used (D_1), first-cycle regenerated (D_2), and second-cycle regenerated (D_3) adsorbents, respectively. When the mass of the O-A-T was increased, the decolorization rate generally declined, but they were all kept above 62% and even reached 68.1%. Moreover, the decolorization rates increased slightly after the second regeneration. The total adsorption capacities of the FS and SL were seemingly inconsistent with these results, which could probably be ascribed to the slight changes in the concentrations of the components in the hydrolysate.

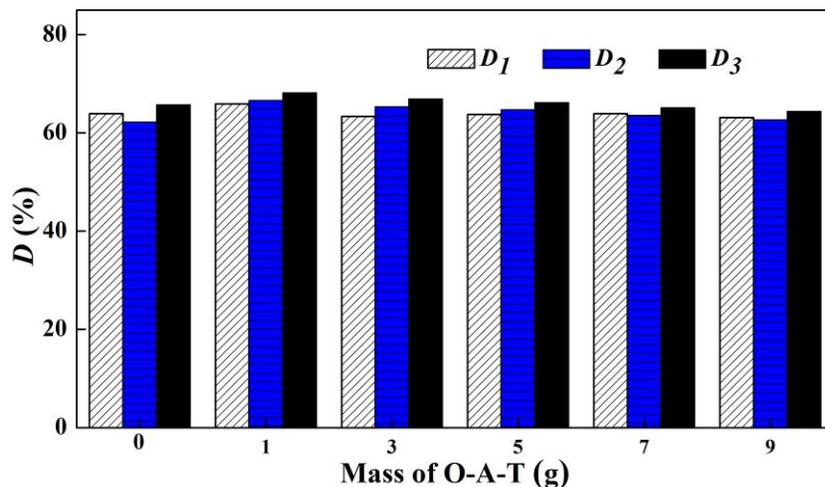


Fig. 7. The decolorization rate of the mixed hydrolysate purified by fresh (D_1), first cycle (D_2), and second cycle (D_3) regenerated PSDM-T prepared with different mass of O-A-T.

CONCLUSIONS

1. Weak polar polymeric resin, PSDM, and its composite absorbent (PSDM-T) were prepared *in situ* using a suspension polymerization method. The optimal feed time of the inorganic ingredient of PSDM-T, O-A-T treated by silane coupling agent KH-570, was the precise moment that the reaction system reached 80 ± 1 °C.
2. The different masses of O-A-T added into the polymer resulted in different pore parameters and adsorption results. Adding a small amount of O-T-A is favorable for hydrolysate purification by PSDM-T. The adsorption properties of PSDM-T superior to PSDM and AB-8. The maximum total removal rate of inhibitors reached about 50%, and the decolorization rates were all above 63%.
3. The PSDM-T displayed a good reusability. A high operational stability indicated that the PSDM-T could successfully be used in a continuous system for the detoxification of hydrolysate.

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